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INVESTIGATION OF COPPER SEGREGATION TO THE Σ5(310)/[001] SYMMETRIC TILT GRAIN BOUNDARY (STGB) IN ALUMINUM

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ABSTRACT

The Σ5 (310)/[001] symmetric tilt grain boundary (STGB) in the face centered cubic (FCC) metal aluminum with 1at% copper has been studied. The model grain boundary has been fabricated by ultra-high vacuum diffusion bonding of alloy single crystals. The segregation of the copper has been encouraged by annealing the sample after bonding at 200 °C. TEM samples of this FCC-material were prepared with a new low voltage ion mill under very low angles.
The atomic structure of the Σ5(310)/[001] STGB for this system was modeled with electronic structure calculations. These theoretical calculations of the interface structure indicate that the Cu atoms segregate to distinct sites at the interface. High resolution electron microscopy (HRTEM) and analytical electron microscopy including electron energy spectroscopic imaging and X-ray energy dispersive spectrometry have been used to explore the segregation to the grain boundary. The HRTEM images and the analytical measurements were performed using different kinds of microscopes, including a Philips CM300 FEG equipped with an imaging energy filter. The amount of the segregated species at the interface was quantified in a preliminary way. To determine the atomic positions of the segregated atoms at the interface, HRTEM coupled with image simulation and a first attempt of a holographic reconstruction from a through-focal series have been used.

INTRODUCTION

We have chosen a model grain boundary to investigate the segregation of an impurity to distinct sites in the boundary. Specifically, we use copper segregation in a aluminum Σ5(310)/[001] STGB. The phenomenon of segregation is of long standing scientific interest and has been studied extensively, both theoretically as well as experimentally [1, 2]. The comparison between theoretically predicted grain boundary structures and experimentally determined structures is important, especially for understanding the mechanical and physical properties of materials. Special grain boundaries such as the Σ5(310)/[001] STGB can give us first insights into the more general behaviour of grain boundaries. Studying a variety of bicrystals in different orientations may lead us to predict the properties of polycrystalline materials but certainly gives us a greater understanding of the complex behaviour of these real materials. The ability to choose and manipulate the occurance of special grain boundaries in a polycrystal can improve the material performance and can be used to design and engineer materials for optimum properties by using the knowledge of structural/properties relations for the grain boundaries.
With the controlled fabrication and preparation of bicrystals we are able to determine composition, structure and morphology of grain boundaries which depends on geometry, crystal orientation, impurity concentration and temperature. The limiting factor in this approach is the ability to fabricate well defined, precisely oriented interfaces, which is enabled here with the UHV Diffusion Bonding Machine [3].

EXPERIMENTAL DETAILS

The single crystal of Al-1at%Cu was grown by the Bridgeman technique in a graphite mold with a growth axis of [001]. The crystal was oriented for cuttting using Laue backscatter X-ray diffraction. The surfaces to be bonded were ground and polished to be co-planar with (310) to within 0.1°. This precision can be achieved by mounting the crystal slices in a specially designed goniometer equipped lapping fixture. The Σ5(310)/[001] STGB is then formed by a mutual misorientation of 180° of one crystal with respect to the other about an axis normal to the bonding faces. Details of this process are explained and discussed elsewhere [4].
The ultra-high vacuum (UHV) diffusion bonding process bonds the bicrystal under highly controlled environmental conditions. The two single crystals were bonded in the solid state at a temperature of 540 °C with a constant applied pressure of 1.0 MPa for 8 hours. Afterwards the bicrystal was annealed for 100 hours at 200 °C using a flowing Argon atmosphere of approximately 1 bar. For the TEM sample preparation, a 3 mm rod was cut by wire electric discharge machining (EDM) out of the bicrystal parallel to the interface. The rod was then cut with a diamond wire saw in 200 to 300 μm thick slices to create the 3 mm disks required for TEM. Standard grinding, polishing and dimpling were additionally performed. A new type of ion mill was used to gently thin the material. With this ion mill (Linda Technoorg IV3H/L), one can use in the beginning a high voltage gun operating between 2kV and 10kV and afterwards, for the finishing step, an ion gun operating at a low energy between 200 V and 2kV. Additionally one is able to choose a low incident ion beam angle of about 5 °. The material of our investigation was thinned for 3 hours with the high energy gun at 2kV from both sides and finally for 1 hour with the low energy gun at 200V and 5° incidence angle with liquid nitrogen cooling. The advantage and the improvement of the TEM samples by using double sided, low angle and low energy thinning has been shown by Strecker et al. [5]. The result and the improvement of ion beam thinning under these conditions can be clearly seen in the HRTEM image in Figure 4a where the surface topography is homogeneously flat over the whole imaged region. Additionally, samples were prepared using conventional jet polishing with solutions and conditions normally preferred for preparing TEM samples of metals and metal alloys.
The investigations were performed primarily using the recently installed Philips CM 300 FEG ST TEM at Lawrence Livermore National Laboratory (LLNL). This microscope operates with a field emission gun at 300 kV and is equipped with a SuperTwin objective lens (ST, C_s = 1.2 mm), a Gatan imaging filter (GIF) with a 2kx2k CCD camera and an EDX detector. Additionally, we performed measurements, particularly the acquisition of the HRTEM through focal series, at the NCEM (National Center for Electron Microscopy) at Lawrence Berkeley National Laboratory with a Philips CM 300 FEG UT TEM (UltraTwin objective lens, UT, C_s = 0.65 mm). The analytical results were partly obtained using a Zeiss EM912 Ω equipped with an Ω energy filter for electron spectroscopic imaging (ESI) and a dedicated VG STEM HB501 for energy dispersive X-ray spectroscopy (EDS), both are located at the Max-Planck-Institut fuer Metallforschung in Stuttgart, Germany.

RESULTS

The relation between grain boundary energy and impurity segregation to the interface have been theoretically calculated for the Σ5 (310)/[001] interface in Al-1at%Cu by using a mixed basis set electronic structure calculation within the Local Density Approximation (LDA) [6]. Figure 1a shows the calculated structure (model) of the interface with the (310) boundary plane in the [001]

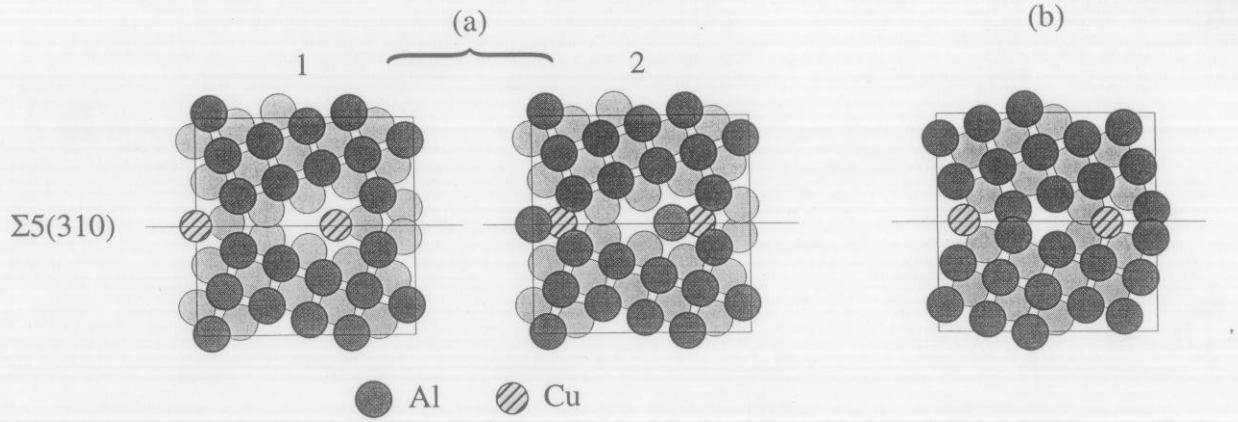

Figure 1: *(a) Atomistic structure (model) for two possible copper positions (b) Structure based on a coincidence site lattice construction.*

viewing direction including the possible positions of the copper atoms. The calculated relaxed structure energies for these two sites are different. One of the calculated sites (2) should be preferred if a size effect is considered to be correlated to the local pressure. The environment of site number (2) is locally compressed while that of number (1) is locally dilated. The overall structure agrees with previous predictions based on pair potential calculations. The Figure 1b represents the structure based on a coincidence site lattice construction (CSL) [7]. The difference between the two lattices is visible. Simulations of the HRTEM images were done by using these two structural models.

To confirm the presence and determine the amount of the segregant, analytical electron microscopy was performed. Three electron spectroscopic images were acquired at the $L_{2,3}$-edge of copper around 931 eV with a 50 eV slit and 50 s exposure time to extract elemental maps (three-window-technique) of the copper distribution [8]. This specific investigation was performed on the Zeiss EM912 Ω, which operates at 120 kV and with a LaB_6 cathode. The overview of the investigated sample position and the resulting elemental map is shown in Figure 2a and b. Figure 2c shows the integrated line profile (integration was performed over 50 pixel lines).

Because of the small amount of the segregated species and the high energy loss of the investigated ionization edge the resulting distribution is heavily dominated by noise. Nevertheless, a bright line (peak in the integrated line profile) which represents the copper at the interface is visible. The copper signal at the edge of the hole is likely due to a preparation artifact. This sample was prepared by jet polishing and the copper might be a remnant of the chemical etching process. The

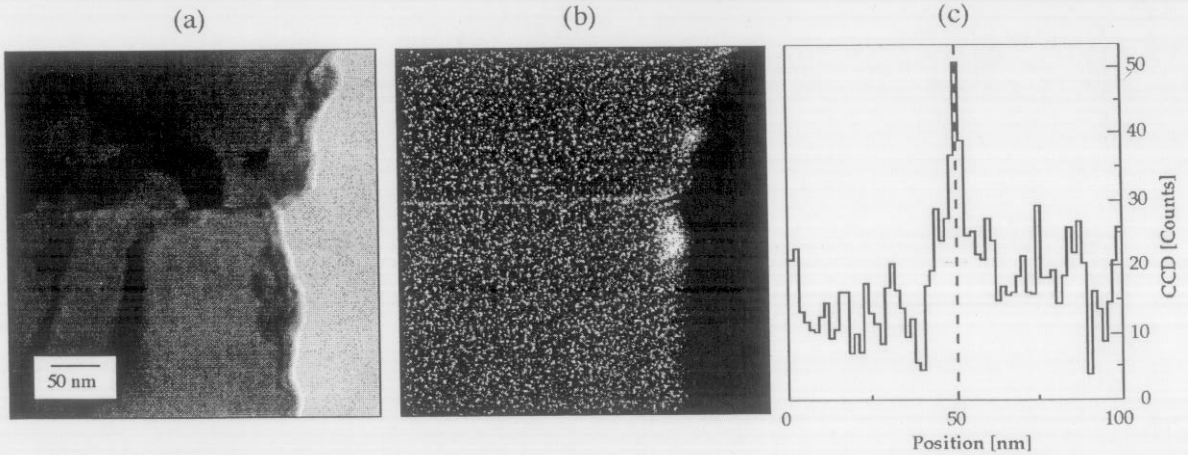

Figure 2: *(a) Bright field image of investigated sample position. (b) Copper elemental map and (c) integrated line profile (50 lines) over the grainboundary in the elemental map.*

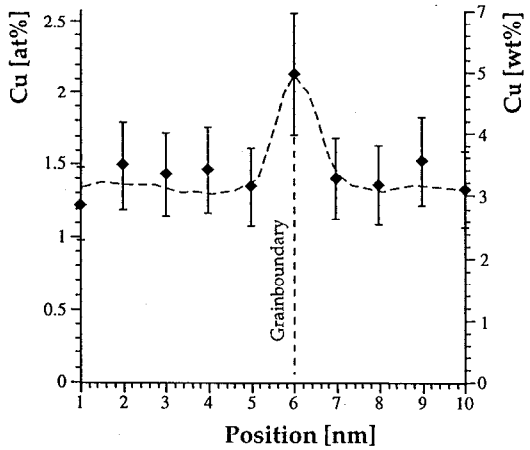

Figure 3: Illustration of an EDS line scan of Cu concentration across the investigated grain boundary.

possibility of sample drift during the acquisition, which might result in a false signal at the interface, was excluded by using several methods for the determination of the real drift between the three acquired images [9, 10]. But, due to the difficulty of investigating copper in such small amounts at the interface with EELS and ESI, the signal in this elemental distribution image (EDI) has to be further confirmed with multiple measurements at different sample positions. Also, the image quality and thus the quality of the result should be improved by using the field emission source at 300 kV in conjunction with the GIF. Precipitates which are rarely present and which might highlight the segregation could be observed, however the sample areas in these regions were too thick to be used for further investigation.

To reveal more precisely the segregation to the grain boundary, EDS line scans were performed and the resulting spectra were quantified. One of the linescans is shown in Figure 3. The amount of the copper in the analyzed volume is doubled ($\approx$ 2 at%) in relation to the bulk concentration of 1 at%. This illustrates clearly the significant segregation of copper to the grain boundary.

High resolution images of the boundary structure were acquired using different consecutive defocus values. To acquire these through-focal series we have automated the acquisition process using the script language of the Gatan Digital Micrograph software. During the acquisition, the stability of the microscope and minimizing the drift of the sample is crucial for allowing image pro-

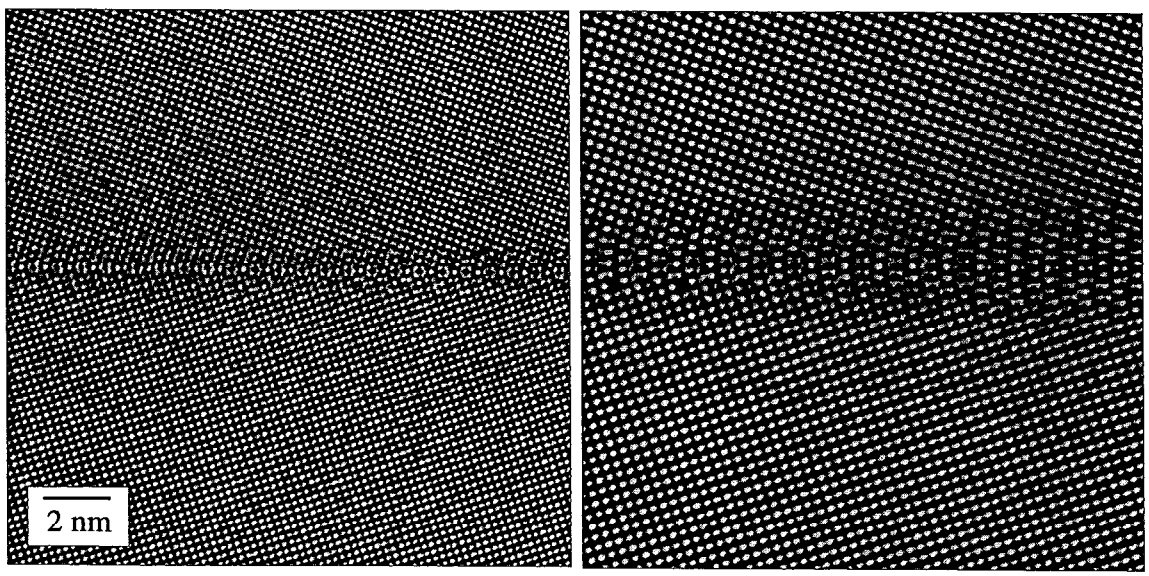

Figure 4: (a) HREM image of Σ5(310)/[001] STGB in Al-1at%Cu. (b) Reconstruction of defocus series.

cessing of the series for holographic reconstruction. The through-focal series can now be acquired by starting the controlling script, without any further manipulation of the microscope. This acquisition procedure is now used routinely at the NCEM at LBL.
The main aim of recording the through-focal series is the possibility of the exit wave reconstruction of the investigated boundary structure. The reconstruction is described in detail elsewhere [11, 12]. Shown in Figure 4a is one of the 30 images of the through-focal series which was obtained with the Philips CM300 FEG UT TEM. The most striking feature of this sample is the homogeneously flat surface of the sample over the field of view and the lack of distortions which are normally present in HRTEM images. This is directly due to the sample preparation with the low energy, low angle ion mill described above. The series was acquired in a defocus range starting at –130 nm. The defocus step was determined to be 2.2 nm. A first reconstruction has been performed and the resulting image can be seen in Figure 4b. The refinement of the reconstruction has to be done by using standard image simulation procedures to determine the exact defocus and imaging parameters at which the image was acquired. The starting structures for these simulations are shown in Figure 1a and b. Image simulation was performed using the EMS software [13]. Figure 5a and b shows two simulated images for nearly the same defocus as in the original image but further simulations and refinements have to be done to improve the fit to the experimental image and the result of the exit wave reconstruction.

CONCLUSIONS AND OUTLOOK

These preliminary findings of segregation in this alloy for this specifically oriented grain boundary revealed the expected segregation behaviour. The structure of the grain boundary and the positions of the copper atom at the grain boundary are not yet determined exactly, but a tendency can be seen in these first results. To obtain more information about the structure in the geometrical and in the electronic perspective we are planning to perform further experiments by using 'Z-contrast' imaging and HREEL spectroscopy. Additionally investigations in the pure (copper-free) aluminum bicrystal will be done to compare the influence of the segregant on the grain boundary structure.
Finally we can say that the TEM sample preparation using a low energy and low angle ion mill can improve the image quality enormously despite the fact that point defects and defect agglomerates are normally produced in the crystals near the surface by ion beams in FCC-metals.

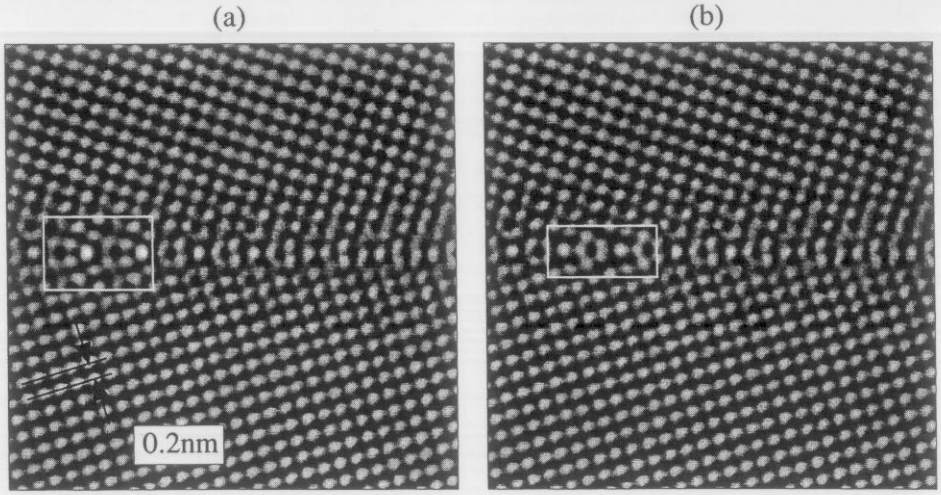

Figure 5: *(a) Simulation for the CSL structure ($\Delta f \approx$ -137nm, t = 4.0 nm). (b) Simulation for the LDA (2) structure ($\Delta f \approx$ -149 nm, t = 4.0 nm).*

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REFERENCES

1. P. Lejcek, S. Hofmann, *Critical Reviews in Solid State and Materials Sciences*, 20 [1] 1-85 (1995).

2. A. P. Sutton, R.W. Balluffi, *Interfaces in Crystalline Materials*, ed. (Oxford University Press, Oxford, 1995).

3. W. E. King, G. H. Campbell, A. W. Coombs, G. W. Johnson, B. E. Kelly, T. C. Reitz, S. L. Stoner, W. L. Wien and D. M. Wilson in *Joining and Adhesion of Advanced Inorganic Materials*, edited by A. H. Carim, D. S. Schwartz and R. S. Silberglitt (Mat. Res. Soc. Symp. Proc. 314, Pittsburgh, PA 1993) pp. 61-67.

4. W. L. Wien, G. H. Campbell and W. E. King in *Microstructural Science*, edited by D. W. Stevens, E. A. Clark, D. C. Zipperian and E. D. Albrecht (Microstructural Science 23, Materials Park, OH 1996) pp. 213-218 ;presented at 28th International Metallography Society Convention.

5. A. Strecker, J., Mayer, B. Baretzky, U., Eigenthaler, T. Gemming, R. Schweinfest, M. Ruehle in *Journal of Electron Micoscopy*, 48 [3] 235-244 (1999).

6. S.M. Foiles, private communication.

7. W. Bollmann in *Crystal Defects and Crystalline Interfaces*, ed. (Springer-Verlag, Berlin, 1970).

8. C. Jeanguillaume, P. Trebbia, C. Colliex in *Ultramicroscopy*, 3 237-242 (1978).

9. J.A. Hunt, private communication.

10. J.M. Plitzko, J. Mayer in *Ultramicroscopy*, 78 207-219 (1999).

11. A. Thust, W.M.J. Coene, M. Op de Beeck, D. Van Dyck in *Ultramicroscopy*, 64 211-230 (1996).

12. W.M.J. Coene, A. Thust, M. Op de Beeck, D.Van Dyck in *Ultramicroscopy*, 64 109-135 (1996)

13. P. A. Stadelmann in *Ultramicroscopy*, 21 131-146 (1987).